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OFFICE OF NAVAL RESEARCH LONDON (ENGLAND)
EUROPEAN SCIENTIFIC NOTES. VOLUME 6, NUMBER 2, (U)
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LONDON

ESN-6-2

6 EUROPEAN SCIENTIFIC NOTES. Volume 6,

Vol. 6, No. 2 ✓

Number 2,

10 S. R. / Aspinall

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London

EUROPEAN SCIENTIFIC NOTES

15 January 1952

Vol. 6, No.2

APPLICATION OF NUCLEAR RESONANCE ABSORPTION TO BETA RAY
SPECTROSCOPY

Dr. G. Lindströmⁿ of the Nobel Institute in Stockholm has applied nuclear resonance absorption techniques to establish an accurate absolute energy scale in beta spectroscopy. He has measured the magnetic rigidities for the F and I lines from Th-B and finds them to be 1388.56 ± 0.15 and 1754.01 ± 0.20 gauss-cm respectively.

Essentially the procedure consists of measuring the line spectra of conversion electrons by means of a small semi-circular beta ray spectrograph placed in a highly uniform magnetic field. The resolution of the spectrograph is such that a variation in magnet current of 0.05 per cent is sufficient to cover the entire instrumental line width. The magnetic field along the trajectory of the electrons is measured very accurately using a proton sample. The mean field experienced by the electrons is then calculated from these measurements. The magnetic rigidity of the line in question may be computed after careful measurement of the distance between source and slit in the beta spectrograph. An alternative and probably more accurate procedure also used by Lindström for determining the rigidity is due to Siegbahn (Arkiv f. Mat., Astro. O. Fysik 30 A, (1944)). This makes use of the fact that the F and I lines arise from conversion of the same gamma ray in the K and L shells. It can be shown that the rigidities can be calculated from a knowledge of the ratio of the magnetic fields for the two lines by using accurately known atomic constants and the K - L energy difference which may be inferred from X-ray measurements.

Lindström["] has also measured the rigidity of the L line of Th-C["]. His value of 2607.17 ± 0.30 gauss-cm agrees within experimental error with the rigidity calculated using the accepted ratio for the rigidities of electrons produced in a converter by annihilation radiation and the L line, and assuming the positron and electron to have equal masses. (The largest positron-electron mass difference consistent with these measurements is 0.01 per cent.

The same nuclear absorption apparatus has been used by Lindström to compare the Larmor frequencies of deuterium, Li⁷, B¹¹, F¹⁹, Na²³, and Al²⁷ with that of the proton. The frequency ratio of deuterium is $\frac{\nu_D}{\nu_P} = 0.15350668 \pm 0.00000012$ using H₂O and D₂O.

Lindström's technique for frequency comparison is interesting. In the case of the deuterium measurement a typical value of the main field was about 6500 gauss. This field was made homogeneous to one part in 40,000 and a sinusoidal 25 cycle modulation field with an amplitude of about 0.3 gauss was superimposed. For this type of comparison the proton and deuteron samples are placed in the same magnetic field. Each experiences a weak oscillating field of the appropriate Larmor frequency which induces transitions in each sample twice per cycle of the modulation field. A double beam oscilloscope is used to display simultaneously the nuclear resonance signals from the two samples, and the oscilloscope is photographed at the moment the radio frequency supplied to the deuterium sample is measured. The main magnetic field and the two radio frequencies are so chosen that the resonances occur at the moments when the modulation field is very close to zero. The linear distance between corresponding points on the two proton resonance peaks on the photograph of one cycle is measured and the corresponding measurement is also made for the deuteron resonances. Because resonance takes place when the modulation field is near zero, the difference between these lengths is proportional to the difference in magnetic field experienced at resonance by the proton and deuteron samples. By repeating this procedure at a number of slightly different radio frequencies for the deuterium sample and plotting the difference in deuterium and hydrogen magnetic fields at resonance as a function of frequency one can determine the radio frequency for the deuterium at which both samples undergo resonance transitions at exactly the same magnetic field.

In order to be sure that resonance for the proton sample occurs at a modulation field very close to zero, the nuclear resonance signal from the proton sample is amplified, rectified, and applied to the grids of two tetrodes. The voltages on the screen grids of these tubes are such that one tube is blocked whenever the modulation field is greater than zero while the other is blocked when it is less than zero. The sense of the difference in plate current of the two tubes indicates whether resonance took place with the modulation field greater or less than zero and the current to the main magnet is automatically varied accordingly. The stabilization of the magnetic field effected in this manner insures that on the average resonance occurs in the proton sample when the modulation field is zero and that for any single cycle the resonances occur very close to zero modulation field.

It is expected that Dr. Lindström will publish an account of his nuclear resonance work in Arkiv för Fysik in the near future.

THE PHOSWICH: A NEW APPLICATION OF SCINTILLATION CRYSTALS

Dr. D.H. Wilkinson of the Cavendish Laboratory, Cambridge, has proposed and developed a modified scintillation crystal which he terms a "phoswich" (phosphor sandwich) and which has valuable coincidence and anti-coincidence properties. It makes use of the fact that there exist phosphors having widely different decay times. The phoswich is a combination of "fast" and "slow" phosphors whose light output is picked up with a single photomultiplier. If a charged particle traverses both phosphors, the fast phosphor gives a high, sharp "spike" on the leading edge of the low, wide pulse due to the slow phosphor.

Experimental Investigation

Wilkinson has used stilbene for the fast phosphor. It has a decay time less than 10^{-8} seconds. For the slow phosphor he used sodium iodide (thallium activated) which has a decay time of about 25×10^{-8} seconds. This combination of phosphors is not an ideal one, but adequate to allow discrimination of the fast and slow pulse. For better discrimination Professor R. Hofstadter of Stanford University has suggested that use of cesium iodide (thallium activated) which has a decay time of 1 microsecond.

Wilkinson was able to demonstrate that stilbene and sodium iodide are transparent to each other's radiation, a necessary condition for their use in a phoswich. A simple

electronic circuit which he has also designed makes possible the recognition of a coincidence or anti-coincidence or anti-coincidence between fast and slow pulses.

Possible Applications

When used as a coincidence device, it should be possible to do with only one photomultiplier those experiments which ordinarily would need two. The anti-coincidence properties also seem promising. By constructing a multiple phoswich consisting of alternate layers of slow and fast phosphors a highly directional detector can be constructed when the electronic circuit is set, for example, to record only slow pulses without "spikes". This would mean that the incident particle would have to travel completely within the slow phosphor. This arrangement, of course, has directivity only in one plane. However, a phoswich constructed in the form of concentric cylinders would be a true telescope.

Another anti-coincidence arrangement of interest would be to immerse a slow phosphor completely in a fast one. In this way a complete anti-coincidence screen could be attained. Such an arrangement might be of value in studying disintegrations by fast neutrons, cosmic ray research, and gamma ray spectroscopy where the electron would be created and stopped in the slow crystal and its energy measured without the disturbing effects of a counter wall.

THE CHARGE SPECTRUM OF COSMIC RAY PRIMARIES

A. Dainton, P. Fowler, and D. Kent of Bristol University have obtained results from a recent high altitude experiment which tend to confirm their earlier findings that Li, Be, and B nuclei are present to a large extent in the primary cosmic radiation. In a study of 100 tracks resulting from particles bearing a charge greater than two, they found more Li, Be, and B than heavier primaries, and in particular the abundance was found to be much greater than the known cosmic abundance of those elements.

Photographic plates were flown at 70,000 ft in a balloon flight in England last summer. A light-weight apparatus was used where a vertically placed G-5 emulsion 400 μ thick, faced a C-2 emulsion 200 μ thick. Tracks of heavy primaries could be traced through both emulsions so as to allow counts of δ -rays in the G-5 and grain densities in the C-2 emulsion. These were combined with measurements of the mean angle of scattering to obtain the charge and velocity spectrum in the manner described previously in Phil. Mag. 42, 317 (1951).

Particular attention was paid to the calibration of δ -ray counts and grain density since the present controversy on the existence of Li, Be, and B in the primary radiation centers on whether grain density and δ -ray counts obey Mott's formula, i.e., whether they are both proportional to Z^2/v^2 . A study of protons and α -particles coming to rest in the C-2 emulsion verified that the relation (grain density $\propto dE/dx$) applies up to 50 grains/50 μ . Similarly, using α -particles coming to rest in the G-5 emulsion, they were able to show that the density of δ -rays having >3 grains was proportional to dE/dx up to about 15-20 δ -rays/100 μ (corresponding to the track of a relativistic Ne nucleus). Above this δ -ray density, the core of the track begins to thicken and other techniques, possibly photo-electric contour tracing of the track, would appear to be more useful.

On the basis of these calibrations it has been found that within the stated limits grain density is proportional to δ -rays density which is in turn proportional to $Z^2/v^{1.46}$. This relation, which holds over a wide range of values of Z and velocity, was then used to identify the primary particles.

CHEMICAL CONSTITUTION OF COENZYME A

A report on the structure of Coenzyme A was made by Drs. James Baddiley and E.M. Thain of the Lister Institute of Preventive Medicine, London, at a meeting of the Chemical Society on November 1, 1951.

Lipmann and his colleagues (J. Biol. Chem. 167, 869 (1947); 177, 97 (1949); J. Amer. Chem. Soc., 72, 4838 (1950)) have shown the coenzyme molecule to consist of pantothenic acid linked to adenosine, together with three molecules of phosphoric acid and a sulfur compound. The last-named component has now been identified by Baddiley and Thain as aminoethyl mercaptan.

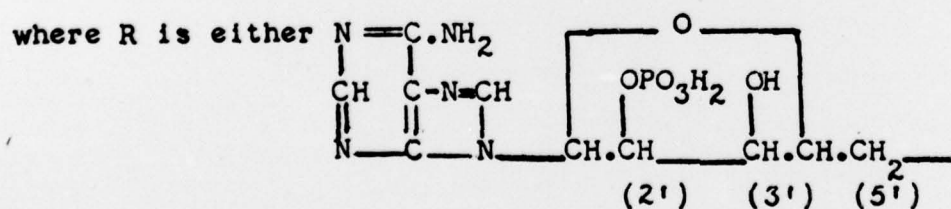
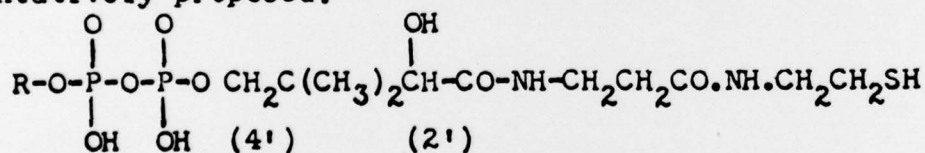
The participation, recently suggested by Lynen and Reichert (Angew. Chem. 63, 47 (1951)), of the sulfhydryl group in the biochemically acetylating function of the coenzyme by the transitory formation of a thiolacetic ester, now appears to be a special case of a more general reaction; the three thiolacetates $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{NHCOCH}_3$ and $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{NHCOCH}_2\text{CH}_2\text{NHCOCH}_3$ have been synthesized and found to be active acetylating agents towards ammonia or hydroxylamine. Evidence in support of this view has also recently been adduced by Kuhn and Quadbeck (Ber. Deut. Chem. Ges. 84, 844 (1951)) who have observed that acetamidoethyl

thiolacetate (the second compound formulated above) reacts with aniline to yield acetanilide and acetamidoethyl mercaptan.

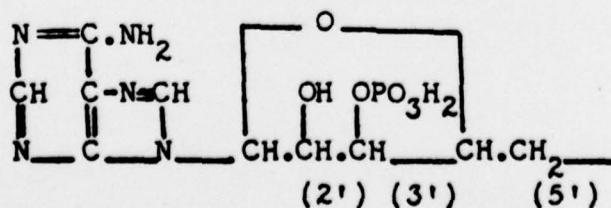
Baddiley and Thain also reported experiments from which the location of the phosphate groups in Coenzyme A can be deduced. Hydrolysis of the coenzyme under mild conditions, followed by separation of the products on paper strips, indicated the formation of pantothenic acid 4'-phosphate, chromatographically indistinguishable from the synthetic compound prepared (J. Chem. Soc. 1951, 246) by an unequivocal method. Neither the 2'-phosphate nor the 2'4'-diphosphate could be detected (J. Chem. Soc., 1951, 2253). The purine moiety was recovered as adenosine-5'-phosphate.

As coenzyme A is split by a dinucleotidase, its adenosine and pantothenic groups are presumably connected through a pyrophosphoryl group (Baddiley and Thain, Chem. and Ind. 1951, 337). The location of the third phosphoric acid groups has been inferentially assigned to either the 2' or the 3' position of the adenosine because the coenzyme yields no dialdehyde when oxidized by periodate.

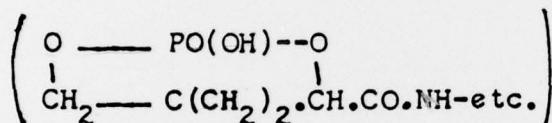
On the basis of the above considerations the following alternative structural formulae for coenzyme A are tentatively proposed:



or



It is, however, possible that Coenzyme A (which has not been obtained in crystalline condition) may contain, in addition, a small unidentified group on the oxygen atom at position 2' of the pantothenic moiety. Novelli, Flynn, and Lipmann have reported (J. Biol. Chem. 177, 493 (1949)) that an enzymatic fission product of coenzyme A, thought to be pantothenic acid 4'-phosphate, stimulates the growth of Acetobacter suboxydans, but the synthetic 4'-phosphate of pantothenic acid is inactive in this respect, as are also the 2'-phosphate, the 2', 4'-diphosphate, and the cyclic 2',4'-phosphate,



(Contributed by the State Department Science Office.)

THE SUBLIMATION ENERGY OF CARBON

Recent experiments by Professor Paul Goldfinger and his collaborators (Brussels) clearly indicate that the sublimation energy of carbon is 141 Kcal/mole. The experiments which are still in progress utilize a new apparatus in which the rate of evaporation from a hot surface and the rate of effusion from a Knudsen cell are simultaneously and independently measured in the temperature range 2400 - 2800° K.

The ratio of cell orifice to total surface was varied between 1/24,000 and 1/300. Experiments are in progress with a ratio of 1/60. The results indicate that the accommodation coefficient of carbon on hot graphite is very much smaller than unity and falls in the range 0.003 to 0.0003. The experimental results on the rate of evaporation are in excellent agreement with the results of previous investigators.

It should be noted that the sublimation energy obtained in this work by direct measurements is in good agreement with the most recent results and conclusions of workers using the electron impact approach (cf. H.D. Hagstrum (Rev. Mod. Phys., 23, 202 (1951)).

A short note on this work will appear in J.Chem. Phys. and the full details will be published in the Bull. Soc. Chim. Belg. Further details can also be found in Technical Report ONRL-3-52, available from the Technical Information Division, Code 250, Office of Naval Research, Washington 25, D.C.

FLUORESCENT COMPOUNDS OF PROTEINS

A novel method for the determination of the molecular weight of proteins has been developed by Dr. Gregorio Weber of the Sir William Dunn Institute of Biochemistry, Cambridge University. This depends upon the principle that when solutions of fluorescent substances are illuminated by polarized light, only those molecules which are oriented in an appropriate direction will be excited by photons. In the case of small molecules there is a time interval of 10^{-8} seconds between absorption and emission, during which period the orientation deteriorates. The underlying theory was originally developed by Perrin, and is treated by Pringsheim in his book on fluorescence and phosphorescence.

Weber bases his work on the experimentally justified assumption that whereas the lifetime of the excited state is independent of molecular dimensions, with large molecules the rate of depolarization depends on the rate of disorientation by Brownian motion, rotation, and diffusion. This rate depends, in turn, upon the molecular volume. That the viscosity of the medium also influences the duration of the excited state has been demonstrated for simple fluorescent compounds by studying them in pure water at different temperatures and in aqueous glycerol of varying concentration.

Fluorescent derivatives of high molecular weight, prepared by coupling proteins with 1-dimethylaminonaphthalene-5-sulfonyl chloride, showed delays in fluorescence decay proportional to the accepted values for the molecular weights of the proteins. However, the "dye" does not necessarily have to be attached by covalent bonds, for the effect is observed with dyes reversibly adsorbed to serum albumin.

D.J.R. Laurence, a former student of Dr. Weber, now working in the Postgraduate Medical College of the University of London, finds that when increasing quantities of serum albumin are added to a solution of 1-naphthylamine-5-sulfonic acid, the percentage polarization of the fluorescent light is directly proportional to the amount of protein until a limiting ratio is reached. This observation makes possible a new technique for the determination of the influence of pH, salts, and surface active agents on the adsorption isotherm of such a system.

In the course of these studies it was observed that addition of the serum albumin causes a characteristic change in the color of fluorescence from dull green to bright blue.

At the same time the absorption maximum is shifted from 320 to 330 mμ. These effects appear to be characteristic of serum albumin and do not take place with serum globulins nor with egg albumin until these proteins are denatured.

Other fluorescent compounds act similarly. o-Acridylbenzoic acid exhibits analogous changes in fluorescence color and absorption spectrum, the intensity of its fluorescence being simultaneously reduced to one-tenth. Fluorescein is quenched to one-quarter and its absorption maximum is shifted from 495 to 505 mμ. The methyl ester of fluorescein shows an even greater shift of absorption, namely from 495 to 515 mμ.

Fluorescence polarization offers the possibility of a novel method for the determination of the albumin: globulin ratio, since serum albumin is the only serum protein that exhibits these changes. On the other hand, analogous effects are brought about by cetyltrimethylammonium bromide and by 90 per cent dioxan, and this suggests that a low dielectric constant may be an important factor. This may likewise be involved in the case of serum albumin, which contains relatively low proportions of hydroxyamino acid groups. (Contributed by the State Department Science Office.)

FIRST INTERNATIONAL PHARMACOPOEIA

The first international pharmacopoeia has been published by the World Health Organization. Work was started in 1937 by an international Technical Commission of Pharmaceutical Experts organized under the auspices of the League of Nations and perpetuated since 1947 by the World Health Organization. The American member of the Commission is Dr. E. Fullerton Cook, Philadelphia, of the Committee of Revision of the United States Pharmacopoeia.

The International Pharmacopoeia contains descriptions of some 200 therapeutic and diagnostic drugs common to several countries. The appendices contain lists of reagents and test solutions, tests for purity of preparations and for determinations of potency and therapeutic value, tables of weights and measures, tables of atomic weights, and tables of usual and maximum doses.

Latin is used for the international title nomenclature, with only one name used, and only the more important synonyms mentioned. English and French editions have been published

and a Spanish edition will be available soon.

A second volume of the Pharmacopoeia now in preparation will contain monographs on newer drugs, including antibiotics, which were not included in the first volume due to failure of agreement among the members of the Commission and the rapid progress being made in development of these substances. Other monographs and appendices will deal with certain tinctures and tablets, injection preparations, and sterility tests.

MICROBALANCES

A "Report of a Symposium on Microbalances" has recently been issued by the Royal Institute of Chemistry. It contains papers by G.F. Hodsman, David W. Wilson, and Hamad M. El-Badry delivered at a symposium on 22 September 1951 in Nottingham. Copies may be obtained from the Institute, 30 Russell Square, London, W.C.1.

TECHNICAL REPORTS OF ONRL

The following reports have been forwarded to ONR, Washington, since the last issue of ESN. Copies may be obtained from the Technical Information Division, Code 250, Office of Naval Research, Washington 25, D.C.

- ONRL-122-51 "International Symposium on Abrasion and Wear, Rubber Foundation, Delft, Holland, November 14-15, 1951" by George J. Szasz
- ONRL-127-51 "The Laboratoire Dauphinois d'Hydraulique of the Etablissements Neyrpric, Grenoble" by F. Joachim Weyl
- ONRL-128-51 "A Colloquium on Non-Linear Vibrations" by F. Joachim Weyl
- ONRL-130-51 "Basic Research on Combustion, Detonation, and Shock Waves at the Laboratoire de Recherches Techniques de Saint Louis of the Direction des Etudes et Fabrications d'Armement" by F. Joachim Weyl
- ONRL-1-52 "The Characteristics of Tritanopia" by Henry Imus
- ONRL-3-52 "The Sublimation Energy of Carbon" by George J. Szasz

PERSONAL NEWS ITEM

W.D. Wright, Professor of Technical Optics at Imperial College, London, will be in the United States from 5 February to 16 April 1952. On 7 February he will present a paper to the Inter-Society Color Council, "Seeing Color Differences". At the Spring Meeting of the Optical Society, 20 - 22 March 1952, he will deliver the Adolph Lomb Memorial Lecture, "The Characteristics of Tritanopia". Dr. S.S. Ballard, Dept. of Physics, Tufts College, Medford, Mass., is arranging visits to New York, Washington, Chicago, Detroit, Cleveland, Rochester, and Ottawa.

Prepared by the Scientific Staff
Submitted by Dr. S.R. Aspinall
Deputy Scientific Director

Philip D. Lohmann

PHILIP D. LOHMANN
Captain, U.S.N.

Assistant Naval Attache for Research

